Quantum theory of solvent effects on electronic spectra: Predictions of the exact solution of the mean spherical model

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A microscopic quantum statistical mechanical theory for the solvent modification of the electronic spectra of nonpolar solutes is developed. Attention is focused on the solute frequency shift as a function of molecular parameters, solvent dielectric constant, and density. Comparison of the predictions of the quantum theory and dielectric continuum models (Onsager–Böttcher and Wertheim) based on the macroscopic reaction field picture are made. Significant differences are found which indicate the importance of solvent structure and nonzero frequency effects absent in the dielectric models. The theory is also applied to several aromatic hydrocarbon molecules in dilute solution with emphasis on the isothermal density dependence of the electronic frequency shift. Generalization of the quantum theory to treat polar solutes is briefly outlined.

I. INTRODUCTION

The effect of dense liquid media on the electronic structure of molecules has been of continuing interest for over a quarter of a century. Most investigations have utilized electronic absorption spectroscopy, where the observed line shapes are generally inhomogeneously broadened Gaussians with maxima significantly red shifted (200–2000 cm\(^{-1}\)) from the gas phase position. Experimental attention has traditionally focused on the solvent and density dependence of the frequency shift of a particular solute electronic transition in dilute solution.\(^{1-6}\) The effect of solute and/or solvent polarity is also of interest.

Theoretical approaches to understanding these phenomena have been almost exclusively based on a second order quantum mechanical perturbation calculation of the solute–solvent coupling characterized by fluctuating point dipole–dipole intermolecular interactions.\(^{7-12}\) The explicit solvent modification of solute electronic properties is treated phenomenologically by employing the Onsager reaction field model\(^{13}\) for a point dipole in a spherical cavity immersed in a dielectric continuum. This approach allows solute spectral behavior to be correlated with the experimental solvent dielectric properties, and has been successful at least at the level of organizing a large body of measurements. However, the reaction field model involves a microscopically undefined parameter, the cavity radius. Molecular dynamics studies indicate\(^{14}\) that identification of this quantity with the solute molecular radius is probably incorrect. In addition, the density dependence, if any, of the cavity radius is entirely unspecified. Also, for obvious physical reasons the treatment of the solvent as a dielectric continuum is not a satisfying approximation. Consequently, a microscopic statistical mechanical theory of the role of solvent structure and many body interactions would seem welcomed.\(^{15}\)

In this paper we consider a fluid composed of spherical molecules interacting via a hard sphere potential. The single molecule electronic degree of freedom is characterized by a fluctuating quantum mechanical point dipole subject to a harmonic restoring force (Drude oscillator). Fluctuating dipoles on different molecules interact via a dipole–dipole coupling. The classical theory for this model was analyzed by Pratt\(^{16}\) and by H"{o}ye and Stell.\(^{17,18}\) They showed that in a variety of approximations (including the mean spherical, single super chain, and related theories), the solvent renormalizations of molecular polarizability, pair correlation functions, and the thermodynamic properties could all be determined in closed form. Using the isomorphism between the path integral formulation of quantum theory and the classical statistical mechanics of polyatomic fluids,\(^{19}\) we have recently extended Pratt’s classical theory to the quantum mechanical case.\(^{20}\) In particular, we determined the exact solutions for the equilibrium thermodynamic and structural properties of this model within the context of the mean spherical approximation (MSA) and related integral equation theories,\(^{21}\) and subsequently we performed an analytic continuation to determine the dynamical predictions of the model.\(^{22}\) The purpose of the present paper is to explore in detail the spectral consequences of this theory for the case of polarizable solute molecules in dilute solution.

The remainder of the paper is structured as follows. In Sec. II the general theory is reviewed and the results relevant to the present paper are summarized and discussed. Calculations of the density and molecular parameter dependence of the solute frequency shift are presented in Sec. III, along with a comparison with the dielectric continuum theories. In addition, application of the theory to experimental measurements of the pressure and solvent dependences of the frequency shift of aromatic hydrocarbons in dilute solution is made. The paper closes with a discussion of our results and future extensions and applications.
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II. THEORY

We consider a polarizable impurity (solute) molecule (at infinite dilution) in a solvent composed of polarizable spherical molecules. The single solvent molecule Hamiltonian is of the form

\[ H_0 = \alpha_0 \omega_0^2 r^2 / 2 + (m - m_0)^2 / 2 \gamma_0, \]

(2.1)

where \( m \) is the total instantaneous dipole moment, \( r \) its conjugate momentum, \( m_0 \) the permanent dipole moment magnitude, \( \alpha_0 \) the static single molecule polarizability, and \( \omega_0 \) the oscillator frequency that characterizes the electronic energy scale. The isolated polarizable impurity Hamiltonian is identical in form to Eq. (2.1) except \( m_0 = 0 \) (we employ the same notation as in Refs. 18 and 19 to denote the impurity polarizability \( \alpha_{\text{imp}} \) and frequency \( \omega_{\text{imp}} \)). The intermolecular interactions are taken to be pair decomposable and contain a spherically symmetric hard sphere potential \( u_0(r) \) plus a dipole-dipole interaction

\[ u(1, 2) = u_0(|r_1 - r_2|) - m_1 \cdot \mathbf{r}_1(r_1 - r_2) \cdot m_2, \]

(2.2)

with

\[ T(r) = (3r^2 - 1) / r^3. \]

(2.3)

Here, \( r_i \) is the position of the center of molecule \( i \), and it is a classical variable. The instantaneous dipole operator of the \( i \)th atom is \( m_i \) and for a solvent molecule it is composed of a permanent dipole component (static, zero frequency component) and a quantum fluctuating part due to molecular polarizability. For simplicity, we consider only the case where the hard sphere diameters of the impurity and solvent molecules have the identical size \( \sigma \).

We begin by considering the equilibrium properties of the pure solvent system. The property of central interest is the single particle polarizability which, according to the mean spherical approximation and related theories, is determined by the self-consistent equation

\[ \alpha^{(s)} = \alpha^{(s)}(1 - 2\alpha^{(s)} E[\alpha^{(s)}]), \]

(2.4)

where \( \alpha^{(s)} \) is the polarizability evaluated at the imaginary frequency \( \omega = \alpha^{(s)} = 2m / \beta \) and \( (\beta \sigma^2)^{-1} \) is the temperature. By definition, \( \alpha^{(s)} \) is the Fourier transform of the fluctuating dipole autocorrelation function \( \beta^{-1/2} \times \delta m_i(0) \cdot \delta m_i(\tau) \) in the imaginary time interval \( 0 \leq \tau \leq i \beta \). In the absence of interactions with the surrounding medium, the polarizability of an isolated molecule is given by

\[ \alpha_0^{(s)} = \alpha_0 [1 + (\omega_0^2 / \omega_0^2)^{1/2}]. \]

(2.5)

The modification of \( \alpha_0^{(s)} \) to \( \alpha^{(s)} \) due to interparticle coupling is described in the theory by the function \( E[\alpha^{(s)}] \), where \( -3(\alpha / \beta) E(\alpha) \) is the dipolar internal energy per particle of a one-component classical system composed of nonpolarizable molecules each with permanent dipole moment \( (3\alpha / \beta)^{1/2} \).

The real time autocorrelation function can be obtained from Eq. (2.4) by replacing \( \omega^{(s)} \) with \( z = i \omega - \epsilon \), letting \( \epsilon \rightarrow 0^+ \), and following standard analytic continuation procedures as discussed in Ref. 19. One obtains

\[ \lim_{\epsilon \rightarrow 0^+} \alpha^{(s)}(z) = \alpha^{(a)}(\omega) + i \alpha^{(a)}(\omega), \]

(2.6)

where the variable \( \omega \) now refers to the frequency of the real time Fourier transform. The fluctuation-dissipation theorem allows the determination of the real time Fourier transform of the fluctuating dipole autocorrelation function through knowledge of \( \alpha^{(a)}(\omega) \).

Explicit implementation of this procedure requires specification of \( E(\alpha) \). A simple approach employs asymptotic arguments to construct the Padé form

\[ E(\alpha) = a\alpha / (1 + b\alpha), \]

(2.7)

where \( a \) and \( b \) are in general functions of both density \( \rho \) and temperature. The above form reproduces the correct behavior in both the small and large \( \alpha \) limits. For the hard sphere \( u_0(r) \) considered here, the coefficients \( a \) and \( b \) can be determined from the small and large \( \alpha \) properties of the dipolar hard sphere fluid. The latter are accurately represented by the free energy formula of Rushbrooke, Stell, and Hynne (RSH). Such a procedure yields

\[ a = 4\pi \rho \sigma^3 I_2(\rho \sigma^2), \]

(2.8a)

\[ a / b = E_\omega = 4\pi \rho \sigma^3 I_2(\rho \sigma^2) / I_2(\rho \sigma^2). \]

(2.8b)

where the functions \( I_2(x) \) and \( I_2(x) \) are given in Ref. 20. In the large and small \( \alpha \) limits our simple Padé expression for \( E(\alpha) \) [Eq. (2.7)] reproduces exactly the numerical results of RSH. For intermediate values of \( \alpha \), differences between our Padé and the RSH formula are never greater than 11% over the entire range of liquid densities. The principal results obtained from the present theory should not depend sensitively on the specific form of \( E(\alpha) \).

By employing Eq. (2.7) and the analytic continued version of Eq. (2.4) one can derive explicit formulas for the solvent absorption \( \alpha' \) and dispersion \( \alpha'' \). As demonstrated in Ref. 19, the solvent absorption is nonzero only in a finite frequency region \( \omega_\ast \leq \omega \leq \omega_\ast \), where

\[ \omega_\ast = \omega_\ast[1 + \alpha \beta + (8 \alpha_0 \beta)^{1/2}] \]

(2.9)

Therefore, the character of the solute absorption will depend on whether the solute frequency \( \omega_\ast \) is close (possible inside) or far away from the solvent absorption band. We consider only the latter nonresonant case since it is generally the experimentally relevant situation and corresponds to spatially localized solute electronic states. [See Ref. 19 for a discussion of the resonant case and possible experiments to probe solute electronic state delocalization phenomena.] For the nonresonant case, only the solvent dispersion outside the absorption band is relevant. With the procedure sketched in Ref. 19, one finds that outside the band this dispersion is given by

\[ \alpha''(\omega) = -\alpha_0 B(\omega) / A(\omega) \left[ 1 - 2(\omega / \omega_\ast)^{1/2} \right], \]

(2.10)

where

\[ A(\omega) = 2\omega \rho \left[ (\omega / \omega_\ast)^2 - 1 + 2\alpha \rho B(\omega) \right] \]

(2.11a)

\[ B(\omega) = (\omega / \omega_\ast)^2 - 1 + \alpha \rho \]

(2.11b)

This result may be combined with the MSA expression

for the renormalized polarizability of an impurity dissolved in the liquid at infinite solute dilution\(28,19\):
\[
\alpha_J(\omega) = \alpha_{J0}(\omega)/(1 - 2\alpha_{J0}(\omega) E[\alpha(\omega)])
\]
(2.12)
By analytic continuation to real frequencies, one obtains for the nonresonant case \(\omega < \omega_0\) or \(\omega > \omega_0\),
\[
\alpha'_J(\omega) = \alpha_{J0}(\omega)/\omega \quad (\omega - \Omega),
\]
(2.13)
where \(\Omega\) is a root of
\[
0 = \omega^2_\Omega - \omega^2 - 2\alpha_{J0}\rho_0^2 \epsilon_\infty E'(\omega)
\]
(2.14)
and
\[
E'(\omega) = \alpha(\omega)/[1 + b\alpha(\omega)].
\]
(2.15)
Since the solute electronic absorption spectrum is proportional to \(\alpha^2_J(\omega)\), it is clear from Eq. (2.13) that the frequency maximum is \(\Omega\). The frequency shift is defined as
\[
\Delta \Omega = \Omega - \omega_\Omega
\]
(2.16)
Having assumed the impurity frequency \(\omega_\Omega\) is far from the solute absorption band, the transcendental Eq. (2.14) can be solved approximately with virtually negligible error to yield
\[
\Delta \Omega = \omega_\Omega [1 - 2\alpha_{J0}\rho_0^2 \epsilon_\infty E'(\omega_\Omega)]^{1/2} - \omega_\Omega
\]
(2.17)
It is convenient to define a dimensionless frequency shift as
\[
\Gamma = \Delta \Omega/\omega_\Omega = (\alpha_{J0}/\rho_0^2, \alpha_{J0}/\rho_0^3, \omega_\Omega/\omega_\Omega)
\]
(2.18)
where the dependence on the four dimensionless parameters has been explicitly indicated. Note that in the often applicable perturbative regime \(\Gamma \ll 1\), the dimensionless shift is a simple linear function of the solute polarizability parameter \(\alpha_{J0}\). The remaining parameter dependence is not as simple and will be explored in detail in the next section.

Several features of general interest concerning these results should be noted. Within the context of our specific model (harmonic Drude oscillator and mean spherical approximation), the present results are exact, non-perturbative expressions for the spectral properties. The temperature independence of our results is a consequence of the specific model and the use of hard sphere interactions. The absence of a nonzero spectral linewidth is a result of both the mean field nature of the mean spherical approximation and the use of a harmonic (Drude) model. Removal of either feature\(^{28,19}\) would result in a small but finite width.

The classical limit of the present theory is obtained by evaluating the solvent dispersion \(\alpha'(\omega_\Omega)/\omega_\Omega\) for \(\omega_\Omega/\omega_\Omega = 0\). In this limit the dimensionless frequency \(\Gamma\) is independent of the solvent and solute transition frequencies as expected for a classical system. Another feature of interest is that the solute spectrum is independent of any solvent permanent dipole moment. This behavior is a consequence of the fact that a permanent dipole moment is a zero frequency (nonfluctuating) property. Within the context of our specific model, the imaginary frequency polarization components decompose into independent modes.\(^{28}\) This precludes any modification of the high frequency impurity dipole fluctuations by the static solvent dipole moment. Theories that go beyond the Drude and/or MSA aspects of the present formalism will allow coupling of the solvent permanent dipole to the impurity polarizability. However, it is interesting to note that several experimental studies\(^{21}\) on nonpolar solvents seem to suggest that solvent polarity is a minor effect that does not introduce any qualitatively new behavior.

Inspection of Eqs. (2.10), (2.11), (2.15), and (2.17), indicates that the solute frequency shift is red \((\Gamma < 0)\) for \(\omega_\Omega < \omega_0\), but blue \((\Gamma > 0)\) for \(\omega_\Omega > \omega_0\).

The interpretation of this behavior for real materials is discussed in the next section.

III. MODEL CALCULATIONS AND APPLICATIONS

Before presenting numerical results and experimentally relevant applications, it is important to discuss the limitations and range of applicability of our model for real materials. There are three general aspects to consider. The first concerns the assumption of spherical molecules and neglect of polarizability anisotropy. The latter simplification can be easily relaxed within the context of our present model but considering the former point does not seem warranted. The spherical molecule assumption is probably reasonable for non-associated liquids since we have considered only long range dipolar interactions which should depend primarily on the gross aspects of particle packing and not the details of molecular shape. Indeed, we have adopted point dipoles and neglected the explicitly repulsive coupling due to charge overlap of extended electronic distributions.

Another consideration involves the existence of only a single energy scale interest in the harmonic Drude oscillator model. Such a description can probably be made realistic for thermodynamic properties and/or a representation of solvent molecule interactions since one can choose the model parameters \((\alpha_{J0}, \omega_\Omega)\) to mimic the real London dispersion forces. Such an approach would associate the electronic energy scale \(\hbar \omega_0\) with the first ionization energy of the solvent molecule. Therefore, for the low lying solute electronic bands generally investigated experimentally, one will be in the \(\omega_\Omega < \omega_0\) regime which leads to a solute frequency red shift. Further support for this approach follows from a second order perturbation theory treatment of the dispersion interaction induced spectral shift.\(^{13,14,46}\) According to that analysis, the solute shift depends sensitively on an oscillator strength weighted average energy characteristic of the solvent molecule. Using the limited available information concerning excited molecular electronic states, this energy usually is of the order of a first ionization energy\(^{6,16}\) and therefore turns out to be much greater than the low lying solute transition energy. Hence a spectral red shift is predicted in accord with experimental observation. However, the existence of many electronic states, transitions between which have very different oscillator strengths, suggests the magnitude of the frequency shift will be sensitive to these
Consequently, our two parameter Drude model cannot be expected to quantitatively predict the magnitude of the solvent induced frequency shift. However, perturbation theory arguments\textsuperscript{20,21} lead us to expect that the relative density and solvent molecule parameter dependence of the above feature should be reliably represented by the model.

A related point is our neglect of molecular vibrational structure and the attendant Franck-Condon considerations. For the electronic frequency shift this should entail very little error since vibrational solvent shifts are generally orders of magnitude smaller than the purely electronic shifts.\textsuperscript{21}

Finally, it should be noted that we have included only induced dipole-induced dipole (dispersion) and solute induced dipole-solvent permanent dipole interactions. For the generally relevant $\omega_{s/1} < \omega_{0}$ case, these lead to a spectral red shift. However, if the solute permanent dipole moment significantly changes on going from the ground to excited electronic state, then additional blue or red shifts can be present.\textsuperscript{8} Due to the harmonic nature of the model used in this paper, such an effect cannot be described. [Sec. however, Sec. IV for a brief discussion of its approximate inclusion.] For this reason we have considered only nonpolarizable solutes. The above omission would be difficult to investigate quantitatively in any event due to our incomplete knowledge of the excited electronic state structure of complex molecules.

All the existing dielectric cavity theories for nonpolar solutes are also subject to the above limitations, in addition to the several extreme approximations discussed in the Introduction.

A. Model calculations and comparison with dielectric cavity theories

Our purpose in this section is twofold. First, we study the dependence of spectral shift on the microscopic parameters of our model including the behavior in the classical limit. These dependences can be probed by performing experiments which vary solutes, solvents, and apply high pressure. Second, a direct comparison with the predictions of the various dielectric cavity theories is made. All the dielectric models are based on representing the solute molecule as a point dipole in a spherical cavity surrounded by a "solvent" of homogeneous dielectric material. In the language of Eq. (2.17), the dielectric approaches are zero frequency ($\omega_{s/1}/\omega_{0} = 0$) theories and the local field function $R(\alpha)$ is calculated using continuum dielectric methods. As a result, the solvent enters the theory only in terms of the macroscopic refractive index. We follow Sullivan and Deutch\textsuperscript{12} and consider two specific dielectric models: Wertheim\textsuperscript{22} and Onsager-Böttcher.\textsuperscript{19,23} The difference between the various models is embodied in the constraints imposed on the "local electric field" experienced by the solute due to the dielectric continuum.\textsuperscript{24} [See Ref. 12 for a more detailed discussion of these dielectric theories.] Traditionally, the Onsager-Böttcher theory has been most often employed to interpret experiments. Its prediction for nonpolar systems is

$$-\Delta \omega = R_{s}^{2}(\epsilon - 1)/(2\epsilon + 1),$$

where $\epsilon$ is the solvent dielectric constant (or optical refractive index squared) and $R_{s}$ the cavity radius. The latter quantity is entirely unspecified by the theory and is generally taken to be a density independent constant, although some workers\textsuperscript{1-4} have assumed $R_{s}^{2}$ is proportional to the density in an effort to obtain better agreement with experiment. This point will be returned to in Sec. III B.

The dielectric theories always predict a red shift of the solute absorption. As discussed above, for the generally realistic case when $\omega_{s/1} < \omega_{0}$ our microscopic theory also yields a red shift. For this reason, all numerical calculations have been performed for the $\omega_{s/1}/\omega_{0} < 1$ regime. However, it is possible that if one could experimentally resolve the condensed phase spectra of highly excited electronic states, the blue shift behavior may be relevant. We simply note that for fixed interaction parameters ($a_{s/1}, a_{0}, p^{2}$) the blue shifts are significantly smaller in magnitude than the corresponding red shift ($\omega_{s/1}/\omega_{0} < 1$) calculation, but increase more rapidly with density than the analogous red shift.

Frequency shift calculations were performed employing Eqs. (2.10), (2.11), and (2.15) - (2.18). Dielectric cavity theory computations were carried out using the formulas\textsuperscript{25} presented in Ref. 12. The solvent dielectric constant was computed using the mean spherical approximation.\textsuperscript{25} Results are displayed in Figs. 1 - 3. As emphasized in Sec. II, the dimensionless frequency shift $\Gamma$ depends on four dimensionless parameters. However, the dependence on $a_{s/1}$ is essentially a simple linear scaling and has therefore not been numerically studied. The remaining three parameter dependences have been investigated individually in Figs. 1 - 3, with the calculations displayed in a relative or scaling form. Several features of general interest emerge: (1) The absolute magnitude of $\Gamma$ depends sensitively on all the parameters, including $\omega_{s/1}/\omega_{0}$. The dielectric theories are, of course, independent of the latter parameter. (2) The relative dependence on a single parameter depends very weakly (typically of the order of a few percent over realistic parameter ranges) on the values of the secondary (fixed) parameters. This behavior is reminiscent of the results of our impurity solvation free energy calculations.\textsuperscript{18} For this reason graphs for only a single choice of the secondary parameters are displayed in Figs. 1 - 3. (3) The relative density dependence is significantly different for the dielectric and microscopic theories, and also is in contrast with the linear $\rho$ behavior predicted by a second order perturbation theory treatment of the dispersion interactions. These differences should be amenable to experimental studies that utilize high pressure.

Another feature of interest is the fact that the continuum dielectric theory predictions are uniquely fixed once the solvent dielectric constant is specified. This of course cannot be rigorously true for any microscopic theory. For our Drude/MSA theory, specification of the nonpolar solvent dielectric constant defines a precise relationship between the two dimensionless param-
FIG. 1. Relative solute frequency shift as a function of solvent polarizability $\alpha_0$ for a particular choice of secondary parameters $(\alpha_{0,1}/\sigma^3, \rho \sigma^3, \omega_{0,1}/\omega_0)$. The Wertheim (W) and Onsager–Büchner (OB) dielectric cavity predictions are contrasted with the Drude/MSA (D) results. As discussed in the text, these results are only very weakly dependent on the secondary parameter values.

FIG. 2. Same as Fig. 1 except here relative solute frequency shift is considered as a function of reduced density $\rho \sigma^3$.

FIG. 3. Same as Fig. 1 except here relative solute frequency shift is studied as a function of $\omega_{0,1}/\omega_0$. The absolute magnitude of the dimensionless frequency shift $\Delta \Omega/\omega_{0,1}$ is also presented for $\omega_{0,1}/\omega_0 = 0$. The absolute magnitude of this quantity can be accurately estimated for other parameter choices by appropriate scaling using Figs. 1–3.

FIG. 4. The upper graph displays the dimensionless solute frequency shift relative to its value $\Gamma_{0,1}$ at $n^2 = 1.69$ (where $n^2$ is the optical dielectric constant) plotted as a function of the Bayliss parameter $n^2/(2n^2 + 1)$. The two dielectric predictions are presented along with two distinct microscopic Drude calculations. The solid line corresponds to $\rho \sigma^3 = 0.8$. The variation of $n^2$ is accomplished by varying the solvent $\alpha_0$. The long-dashed curve corresponds to $\alpha_0 = 0.075 \sigma^3$ and variable density. The lower graph displays the dimensionless solute shift as a function of $\rho \sigma^3$ for two choices of fixed dielectric constant $n^2$. At each density, the value of $\alpha_0$ is chosen to reproduce the fixed $n^2$ value.
TABLE I. Molecular parameters at 25 °C and 1 atm.

<table>
<thead>
<tr>
<th>Solvent properties</th>
<th>( \epsilon )</th>
<th>( \rho a^3 )</th>
<th>( \alpha_0 / \sigma^3 )</th>
<th>( \beta n \sqrt{\gamma} / \sigma^3 )</th>
<th>( \beta n \beta_0 / \sigma^3 )</th>
<th>( \sigma^* (\text{Å}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>1.87</td>
<td>0.847</td>
<td>0.0645</td>
<td>0</td>
<td>411</td>
<td>5.7</td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td>2.66</td>
<td>0.907</td>
<td>0.098</td>
<td>0</td>
<td>436</td>
<td>4.5</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.38</td>
<td>0.904</td>
<td>0.0795</td>
<td>0.02</td>
<td>356</td>
<td>5.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solute properties</th>
<th>Transition ( \omega_{0,t} ) (cm(^{-1}))</th>
<th>( \Omega ) (1 atm)</th>
<th>( \alpha_{0,t} / \sigma^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracene</td>
<td>( ^1 L_a ) 27 590</td>
<td>26 681 (Hexane)</td>
<td>0.0647</td>
</tr>
<tr>
<td></td>
<td></td>
<td>26 125 (Toluene)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>25 975 (CS(_2))</td>
<td></td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>( ^1 L_b ) 29 163</td>
<td>28 931</td>
<td>0.0207</td>
</tr>
<tr>
<td>Benzene</td>
<td>( ^1 L_b ) ≈ 38 525</td>
<td>38 300</td>
<td>0.0133</td>
</tr>
</tbody>
</table>

*aSolvent dielectric constants, densities, and dipole moments were taken from Ref. 27.
Molecular polarizability and first ionization energy \( \omega_0 \) were obtained from Refs. 25 and 29, respectively.

*bGas phase transition frequency for benzene was extracted from measurements in Refs. 2 and 4. Other solute values were taken from Ref. 1(c). For consistency, liquid phase frequencies (and hence frequency shifts) at 1 atm for anthracene and phenanthrene in hexane are taken to be those measured in Ref. 1(c). All other liquid phase frequencies are from Refs. 4 and 5.

*aAdjusted, see the text.

B. Experimental applications

Most experimental investigations of the solute frequency shift as a function of molecular environment have involved variable solvent studies. From a theoretical point of view, this approach is not optimum since different solvents introduce not only different dielectric properties, but also variable liquid structure (i.e., particle packing) due to molecular shape effects. A cleaner and more definitive test of the theories is obtained from the application of high pressure as a tool to vary the solute environment. We have therefore applied our theory to the high pressure experiments on dilute solutions of aromatic hydrocarbons performed by Okamoto and Drickamer.\(^{3,4}\)

Numerical implementation of the theory entails specification of five parameters: \( \rho a^3 \), \( \alpha_0 / \sigma^3 \), \( \alpha_{0,t} / \sigma^3 \), \( \omega_0 \), \( \omega_{0,t} \). See Table I. In order to mimic the London dispersion and permanent dipole interactions between solvent molecules, \( \alpha_0 \) and \( \beta n \beta_0 \) were taken to be the known single molecule polarizability and first ionization energy, respectively. Using the experimental density, the hard sphere diameter was varied to reproduce the experimental solute dielectric constant (as computed theoretically with the MSA\(^{\text{12h}}\)). The solute frequency \( \omega_{0,t} \) was taken to be the gas phase electronic transition frequency under consideration, while the solute polarizability density \( \alpha_{b,t} / \sigma^3 \) was adjusted to reproduce the experimental frequency shift in liquid hexane at atmospheric pressure. Since we are primarily interested only in the pressure (density) dependence of the solute frequency shift, our results are not sensitive to the specific parameter values taken for the impurity Drude oscillator. However, within the context of our Drude model, the isolated impurity electronic structure is uniquely determined by the values of \( \omega_{0,t} \) and \( \alpha_{0,t} \).

Therefore, having chosen \( \omega_{0,t} \) to reproduce the frequency shift of a particular solute transition in a specific solvent, this value can then be used to predict the absolute magnitude of the solute frequency shift in other solvents. The accuracy of these predictions is at least a measure of the consistency of the theory.

We have considered two sets of high pressure experiments: (1) the aromatic hydrocarbons phenanthrene,\(^{4,5}\) anthracene,\(^{4,5}\) and benzene\(^{4}\) dissolved in liquid hexane at 25 °C, and (2) anthracene dissolved\(^{5}\) in carbon disulfide and toluene at 25 °C. The specific electronic transitions considered and the parameters employed are listed in Table I.\(^{27}\) Calculations were performed as a function of density with the results shown in Figs. 5 and 6. There are several points of interest. As previously noted, the traditional Onsager–Böttcher cavity model is not very accurate for these systems, although the assumption that the cavity volume scales inversely with the solvent density\(^{3-5}\) greatly improves the agreement. Curiously, our Drude theory predictions are numerically very close to this modified cavity model. Note also that the dielectric predictions are independent of solute molecule, while the Drude theory exhibits a weak dependence.

The solvent dependence of the frequency shift can be determined for anthracene using the \( \alpha_{0,t} \) value listed in Table I (which was obtained from the hexane experiment). The Drude theory predicts frequency shifts at atmospheric pressure of \(-1263\) and \(-1465\) cm\(^{-1}\) for toluene and carbon disulfide, respectively. The experimental values\(^{30}\) are \(-1465\) and \(-1715\) cm\(^{-1}\), respectively. Analogous dielectric theory predictions can be extracted by choosing the solute dependent constant.
of proportionality, \( k \) of Ref. 12, to reproduce the experimental frequency shift of anthracene in liquid hexane. The calculated results for anthracene in toluene and carbon disulphide are: \( -1121 \) and \( -1303 \) \( \text{cm}^{-1} \), respectively, for the Onsager–Böttcher theory; \( -1172 \) and \( -1425 \) \( \text{cm}^{-1} \), respectively, for the Wertheim cavity model.

Considering the simplifying features of our Drude theory, we view the overall agreement with experiment as adequate and encouraging.

IV. DISCUSSION

We have presented results for solvent effects on the electronic spectra of polarizable solutes obtained from our exact solution\(^{10}\) of the dynamical quantum mean spherical approximation. A comparison with existing dielectric cavity models reveals significant differences which should be accessible to experimental test. These deviations are a consequence of the microscopic fluid structure and statistical fluctuations absent in the continuum theories. Applications to the density dependence of aromatic hydrocarbon frequency shifts indicate the differences are important. Further experiments and calculations are needed to elucidate under what general circumstances deviations from continuum dielectric behavior are significant, but these initial studies cast serious doubt on the range of quantitative applicability of the cavity theories.

![Graph showing relative frequency shift as a function of density. The reference density \( \rho_0 \) is that appropriate to the hexane solvent at atmospheric pressure. Experimental results (Refs. 4, 6) are displayed for the three solutes. The short-dashed line is the Onsager–Böttcher cavity theory prediction modified as described in the text. Quantum Drude results are shown for anthracene (dash–dot line), phenanthrene (long-dashed line), and benzene (long-dashed line). On the scale of the graph the latter two are indistinguishable.]

![Graph showing \( \frac{\rho}{\rho_0} \) vs. \( \frac{\rho_0}{2\pi n^4} \) for toluene and carbon disulphide. The relative solute shift is plotted vs. the modified Rayless parameter. The solid line labeled OB is the standard Onsager–Böttcher cavity model result, while the short-dashed line is its modified version. The solid line is the quantum Drude theory prediction and the experimental measurements (Ref. 5) are represented by the solid circles.]

Extensions of the present theory of impurity electronic absorption can be made in several directions. Many of these were outlined in the beginning of Sec. III. Experimentally, one of the most relevant generalizations would treat polar solutes that exhibit a permanent dipole moment change upon electronic excitation. This modification could be affected by employing an anharmonic (cubic and quartic terms) description of single molecule dipole moment fluctuations. The nonlinearities could then be incorporated in the statistical mechanical part of the calculation in a perturbative or mean field fashion. Extensions of the model beyond the mean field (MSA) level are also possible\(^{12}\) and could allow the question of spectral linewidth to be addressed. The prospect of these and other developments of the model are encouraging for the goal of constructing an accurate microscopic theory of molecular electronic states in condensed phases.

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10An exception to the dielectric continuum approach is the work of Fulton in Ref. 11 where the solvent structure is modeled as a rigid cubic lattice. However, such a representation is still far from a realistic description of a dense fluctuating fluid medium.
20We follow Sullivan and Deutch in Ref. 12 and set the background contribution of other transitions to the frequency dependent solute polarizability ($\alpha_s$) equal to zero.
21Note that the polarizability parameter for anthracene is considerably larger than benzenes and phenanthroene values. This is consistent with the experimental fact that the former transition is significantly stronger (larger oscillator strength) than the latter weak transitions.
25The absolute frequency shift for anthracene in toluene and carbon disulfide at atmospheric pressure were determined from the liquid phase values in Ref. 5 and the gas phase measurements of Ref. 1(c). Such a calculation always involves a certain degree of uncertainty due to frequency calibration differences between the two experiments. The degree of this uncertainty was estimated by comparing the liquid state frequencies measured in Ref. 1(c) with those reported in Ref. 4 for several common systems. The frequencies determined in Ref. 4 were typically 100–150 cm$^{-1}$ smaller than those in Ref. 1(c). Consequently, the experimental red shifts of 1465 and 1715 cm$^{-1}$ reported in the text represent an upper bound.